THE ROLE OF A DISPLACEMENT REACTION

IN THE

KINETICS OF OXIDATION OF ALLOYS

by

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Bachelor of Science   The Pennsylvania State University 1958

A Thesis

Presented to the Faculty of the School of Engineering of
Yale University in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering

May 1961

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ABSTRACT

The oxidation of some copper-zinc alloys and a copper-nickel alloy in pure oxygen at 700°C has been studied to determine the occurrence of a displacement reaction of the type

$$B^{+2} + 2e^- + AO = A^{+2} + 2e^- + BO$$

as proposed by C. Wagner. The formation of BO in the displacement reaction has been shown to occur by observing a change in the oxide scale by metallographic examination and by noting a change in the rate of oxidation as given by the parabolic reaction rate constant. A change in the oxidation rate for several samples was further emphasized by observing the rates during two periods of oxidation which were separated by an isothermal annealing period in an inert gas.

STATEMENT OF THE PROBLEM:

When a pure metal reacts with an oxidizing atmosphere at an elevated
temperature, the kinetics may be described in terms of a parabolic rate
equation when there is formed a compact oxide layer and diffusion of ions
and electrons through the layer is rate determining.[1] The oxidation of an
alloy can be considerably more complex. The thermodynamics of oxidation of
the various alloy constituents, each with different activities, must be con-
sidered. The diffusion rates of the different species through the oxide,
which may consist of more than one phase, will be different, and superim-
posed on these features may be a change in the structural and chemical com-
position of the oxide with time. Structural changes brought about by re-
crystallization which affect the oxidation kinetics have been studied on
the oxide of a pure metal by Meijering and Verheijke[2] and on the oxide of
an alloy by Sartell, Bendel, Johnson and Li.[3]

The role of a displacement reaction has received less attention. The
effect of a displacement reaction on the kinetics of oxidation has been
pointed out,[4,5,6] however, the effect has not been correlated with chemical
and structural changes which occur in an oxide under conditions involving an
oxidation process interrupted by an isothermal anneal in an inert atmosphere.
Such changes are of current theoretical and practical interest particularly
for the development of oxidation resistant alloys for high temperature use.

In order to demonstrate the role of a displacement reaction on the
kinetics of an oxidation process, binary, one-phase alloys whose constit-
uents differ widely in affinity for oxygen are the most convenient to use.
Two such systems, the copper-zinc and copper-nickel systems, are considered,

and for both alloys, the oxidation processes were carried out under one atmosphere of pure oxygen, at 700°C and at 800°C, respectively.

Several investigators[7,8] have determined the amount of copper oxide in the total oxide on brasses of various compositions oxidized under conditions similar to those above. Dunn[7] has shown that all brass alloys which have less than 76 weight percent copper oxidize at virtually the same rate, and the oxide on these alloys consists of essentially pure zinc oxide. See Figure 1. For these alloys, the diffusion of zinc, to the surface through the metal and through the oxide is sufficiently rapid to keep pace with the oxygen reacted on the surface, and the parabolic mode of oxidation is approximately followed. This is shown in Figure 2.

In brasses containing between 76 and 82 percent of copper, the amount of zinc capable of diffusing to the surface becomes less than the amount of oxygen absorbed, and as a result the amount of copper in the oxide increases with the formation of cuprous oxide. The oxidation of these brasses does not follow the parabolic oxidation law.

Brasses which contain greater than 90 percent copper are shown to contain greater than 90 percent copper oxide in their oxides. With the remaining amount of zinc oxide either dissolved or as a finely dispersed mixture in the cuprous oxide, it is then expected that the oxidation rate is governed by the diffusion of cations and electrons across the composite oxide layer. The oxidation of these brasses with greater than 90 percent copper conform to the parabolic oxidation law. In experiments where the oxidation is carried out in pure oxygen, a very thin layer of cupric oxide may form on the outer oxide surface. This CuO layer does not appreciably affect the kinetics for the experiments described.

The deviations from parabolic behavior for certain brasses was attributed by Dunn to a sintering or recrystallization of the oxide, and to confirm his hypothesis, he performed the following experiments. Brass of an unspecified composition was oxidized at 725° C under the following conditions:

EXPERIMENTAL CONDITIONS	CHANGE IN WEIGHT
1. Oxygen absorbed in one hour in pure O_2	9.42 mg.
2. Oxygen absorbed after one hour in O_2 followed by two hours in N_2 followed by three hours in O_2	9.8 mg.
3. Oxygen absorbed in four hours in O_2, uninterrupted	17.2 mg.

The two-hour anneal in nitrogen greatly altered the kinetics of the oxidation reaction. C. Wagner[6] suggested that during the isothermal anneal a displacement reaction occurred where

$$Zn \text{ (in alloy)} + Cu_2O = 2Cu + ZnO \tag{1}$$
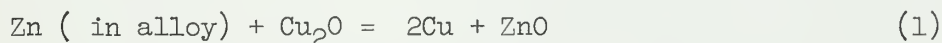
During the oxidation of a hypothetical alloy AB, C. Wagner[4] has stated that such a displacement reaction is possible if the oxide BO, as shown in Figure 3, has a greater affinity for oxygen, i.e., a lower standard free energy of formation, than the oxide AO. He has shown that under such conditions the oxide BO could be expected to grow, even though it is not in direct contact with the oxidizing atmosphere, by the reaction

$$B^{+2} + 2e^- + AO = BO + A^{+2} + 2e^- \tag{2}$$

The free energy of formation of ZnO is less than the free energy of formation of Cu_2O at 700°C. The values are [9]

$$\Delta G^O_{ZnO} = \quad - 60,540 \quad \text{calories / mole}$$

$$\Delta G_{Cu_2O} = \quad - 23,700 \quad \text{calories / mole}$$

Therefore one would expect that reaction (1) would preceed toward the formation of zinc oxide and free copper under the same conditions as those described above for the formation of the hypothetical oxide BO.

Because it is known that the diffusion of zinc ions is slower in zinc oxide than copper ions in cuprous oxide, [10,11,12] a reasonable assumption is that because of the marked differences in the structures of zinc oxide (hexagonal close-packed of the wurtzite type) and cuprous oxide (cubic), copper ions also diffuse more slowly in zinc oxide than in cuprous oxide. In addition, because cuprous oxide and zinc oxide are virtually immiscible, the diffusion of copper in zinc oxide is expected to be very small. If the displacement reaction (1) occurs, the area of contact between the cuprous oxide and the metal alloy would be decreased by the formation of zinc oxide at the interface. Thus the avenues of rapid transit would be blocked, and a decrease in the oxidation rate would be expected to occur as the relatively impermeable envelope developes and increases in thickness. A change in the oxidation rate would be manifested as a change in K_p, the reaction rate constant, in the parabolic equation which may be written as

$$K_p = \frac{d}{dt} \left[\frac{\Delta m}{A} \right]^2 \qquad (3)$$

where $\Delta m/A$ is the weight gained per unit area, and t is the time.

EXPERIMENTAL PROCEDURE:

To check the proposed displacement reaction and to correlate a change
in the oxidation rate with a change in the oxide structure, Cu-Zn alloys
with wt. % Zn = 0.30, 0.15, 0.10 and 0.05 were oxidized in oxygen and
annealed in argon at 700°C. These alloys were chosen because they are
representative samples of the brasses which fall in the three regions shown
in Figures 1 and 2. Also, in order to show the generality of the displace-
ment reaction to other systems, measurements were carried out on a 68 per-
cent copper - 32 percent nickel alloy oxidized in oxygen and annealed in
argon at 800°C.

Specimens 1.15 inch by 0.5 inch were cut from 0.005 inch sheet. *
These metal coupons were annealed in vacuum at a temperature between 375°C
and 400°C, depending upon the composition of the alloy, in order to stabi-
lize grain size and to prevent distortion of the sample during the period
of oxidation. They were polished on emery paper through to 4/0, lapped on
a wheel saturated with Linde A abrasive, and washed with methyl alcohol.
The surface area was determined from micrometer measurements. The oxidation
apparatus is the same as that described in an earlier paper by Pettit,
Yinger and Wagner.[13]

The procedure followed for each oxidation run was to oxidize the sam-
ple in pure oxygen, at a flow rate of approximately 3 liters per hour, for
a period termed the "first oxidation period." For the samples undergoing
continuous oxidation, this period constituted the entire process. In the

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* The brass specimens were kindly furnished by the Chase Brass and Copper
  Company of Waterbury, Connecticut.

interrupted oxidation experiments, the furnace was flushed with argon at the end of the first oxidation period, and the sample was held in a static atmosphere of argon for a determined period of time. The argon was purified by passing it through a furnace containing copper chips at 500°C and successively through tubes containing magnesium perchlorate, Ascarite and magnesium perchlorate. At the end of the isothermal anneal, the argon was evacuated and the flow of oxygen was resumed during a second period of oxidation. All oxidation and annealing temperatures were the same for a particular run, and the temperature was controlled at $\pm$ 3/4°C by a Leeds and Northrup AZAR temperature controller. Curves of each run were plotted as $(\Delta m/A)^2$ versus time in order to obtain K_p, the parabolic reaction rate constant.

In order to follow the changes in structure and composition of the oxide layers as a function of time, representative experiments were terminated and the samples were removed and mounted for metallographic examination.

RESULTS AND DISCUSSION:

Because a change in the kinetics of the oxidation reaction is reflected as a change in the parabolic reaction rate constant, it is possible to qualitatively correlate these values of K_p with the amount of zinc oxide or nickel oxide, as the case may be, present in the total oxide. The values of K_p for the oxidation of representative samples of brasses of various compositions in pure oxygen, at 700°C, both before and after a period of isothermal annealing in argon, are presented in Table I. Because the thickness of the zinc oxide layer is the rate controlling step in the oxidation

of these alloys, the differences in the values of K_p before and after the

isothermal annealing periods of different lengths is a measure of the

relative amount of zinc oxide formed, and hence a measure of the extent to

which the displacement reaction (1) occurs. Rhines and Nelson[14] have

shown that where zinc oxide is associated with cuprous oxide on brasses,

the zinc oxide is pink because of the presence of dissolved copper. This

provides a means of visually identifying the zinc oxide which is formed

with free copper according to the displacement reaction.

A 70-30 brass follows very closely to the ideal parabolic oxidation

law. See Figure 4. One would expect this agreement because, as indicated

in Figure 1, the oxide on a 70-30 brass consists of practically pure zinc

oxide, with a maximum of approximately 3 percent cuprous oxide. X-ray

diffraction analysis of the oxide from several 70-30 brass samples yielded

no evidence of the occurrence of cuprous oxide in the oxide scale. There-

fore, the oxidation rate of these brasses is controlled by the diffusion

of cations and electrons across the relatively impermeable and essentially

pure layer of zinc oxide.

The brasses containing 85 percent copper are representative of those

which exhibit non-parabolic oxidation. See Figure 5. From the graph of

$(\Delta m/A)^2$ versus time, it is seen that the value of the reaction rate

constant decreases during the period of continuous oxidation. The cross-

section of this sample, shown at the end of the three hour oxidation period,

in Figure 6, illustrates the reason for this deviation. The dark oxide at

the oxide-metal interface is actually "pink" zinc oxide which is being

formed by the displacement reaction <u>during the period of continuous oxidation.</u>

As this layer of zinc oxide increases in thickness, the rate constant de-
creases from its initial value for the diffusion of cations across a com-
posite oxide layer, toward the value of the reaction rate constant across
a relatively pure zinc oxide layer, as given by the 70-30 brass.

Figures 7 and 8 show the oxidation curve and cross-sections of an
85-15 brass which was oxidized initially for 90 minutes, isothermally an-
nealed in cleansed argon for one hour to allow the displacement reaction
to occur, and then followed by a second period of oxidation. After the
one hour anneal there is a decrease in the slope* of the rate curve by a
factor of 14. This is caused by the formation of a much thicker layer of
zinc oxide during the period in the inert gas. Note also from the cross-
sections of the oxide of the same sample that in the regions where the
zinc oxide layer is thick and coherent, as in Figure 8(a), the total thick-
ness of the oxide is less than in those regions where the zinc oxide struc-
ture remained in a dispersed state, in a copper-red matrix, as in Figure
8(b). This further emphasizes the impermeable nature of a coherent en-
velope of zinc oxide. The structure shown in Figure 8(a) represents the
more typical found in these studies.

The change in the reaction rate constant under similar oxidizing con-
ditions, but after a two-hour isothermal annealing period in argon, is
shown in Table I. Note that after the two-hour anneal K_p drops to half

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* The data were plotted as

$$(\Delta m/A)^2 \text{ before} + (\Delta m/A)^2 \text{ after} = (\Delta m/A)^2 \text{ second}$$
$$\text{anneal} \qquad \text{anneal} \qquad \text{oxidation period}$$

The first term in this expression is a constant after the isothermal anneal.

the value which was observed after the one hour annealing period. This
difference is to be expected inasmuch as the oxidation rate is controlled
by the thickness of the zinc oxide layer formed by the displacement reaction.

The alloys containing 90 percent or more copper follow closely the
parabolic oxidation law under the conditions of continuous oxidation at
700°C. As previously mentioned and as shown in Figure 1, the oxides formed
on these alloys are composed of cuprous oxide and zinc oxide in approxi-
mately the same ratio as the copper and the zinc concentration in the alloy.
From Table I, it is seen that the value of the rate constant increases as
the amount of cuprous oxide in the oxide layer increases, and it will
approach a limiting value as given by the diffusion of copper ions across
a pure cuprous oxide layer.

The oxidation curve for a 90-10 brass, interrupted by a two-hour
isothermal anneal in argon, is shown in Figure 9. After the displacement
reaction was allowed to occur, the value of the rate constant decreased by
a factor of about 11, less than that for the oxidation of an 85-15 brass
under similar conditions, but certainly significantly enough to show the
occurrence of the reaction. The cross-section of this oxide showed par-
ticles of zinc oxide dispersed in a copper-red matrix.

Recently Sartell, Bendel, Johnston and Li[3] studied the oxidation of
62 percent copper-38 percent nickel alloy. They suggested that the forma-
tion of a nickel oxide phase was due to an inward diffusion of oxygen.

Because the displacement reaction was shown to occur in the absence
of oxygen in copper-zinc alloys, a test was made to determine if this

reaction, and similar results, could be duplicated for a copper-nickel alloy. The standard free energy of formation of nickel oxide is, at $800^{\circ}C$, 10,700 calories per mole less than that for cuprous oxide, and the diffusion of nickel ions through nickel oxide has been shown[15] to be slower than the diffusion of copper ions through cuprous oxide.

A 62 percent copper-38 percent nickel alloy was made following the procedure of Sartell, et al, and the samples were prepared and oxidized at $800^{\circ}C$ in the same manner as that for the copper-zinc samples previously discussed, except, because of a smaller difference in the standard free energy of formation of the two oxides, a four-hour isothermal anneal in argon was utilized. The initial period of oxidation was purposely kept short (30 minutes) in order to restrict virtually all of the displacement reaction to the annealing period, in order to emphasize more vividly its occurrence.

A curve of the oxidation rate and a cross-section of the oxide before and after the isothermal anneal are shown in Figures 10 and 11. Although the value of K_p is not constant during the second period of oxidation, but rather tends, ultimately, toward the value of K_p for the first oxidation period, the fact that there is a change in the slope is indicative of some change in the oxide structure. In Figure 11(a), the cross-section of the oxide at the end of the first period of oxidation is seen to consist of three distinguishable layers. The outer black layer is a thin film of cupric oxide which forms by the oxidation of cuprous oxide. The middle oxide layer is cuprous oxide and the oxide at the metal-oxide scale interface is a cuprous oxide-nickel oxide layer which has a dark orange tint

indicating the presence of free copper in solution in the oxide. This
dark oxide layer forms, in a manner analogous to the formation of the
"pink" oxide layer on the Cu-Zn alloys, by the displacement reaction

$$\text{Ni (in alloy)} + Cu_2O = NiO + 2Cu \tag{4}$$
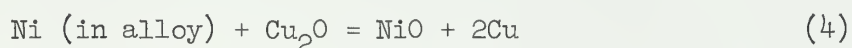
which has occurred during continuous oxidation by the outward diffusion of
cations and electrons. Any structural changes which may have occurred in
the thin cupric oxide layer during this short period of oxidation have not
been considered.

The oxide cross-section after a four-hour isothermal anneal in argon
is shown in Figure 11(b). Microscopic examination reveals numerous areas
of free copper in a matrix of nickel oxide, both of which were formed by
the occurrence of the displacement reaction to a large extent during the
period in the inert gas. It is noted that the interface between the com-
posite oxide and the cuprous oxide did not shift via the displacement re-
action during the anneal and it is believed that because of the porosity
in the inner layer, the nickel ions were unable to migrate to the cuprous
oxide layer. The difference in specific volumes of cuprous oxide
(23.9 cm^3/mole) and nickel oxide (9.9 cm^3/mole) provides a possible ex-
planation for the porosity.

SUMMARY AND CONCLUDING REMARKS:

A displacement reaction has been shown to occur during the oxidation
of alloys in which the values of the free energies of formation of the
oxides of the individual constituents are different. The displacement
reaction was manifested as a change in the parabolic reaction rate constant,

which was shown to decrease as the more impermeable oxide layer was formed. It was shown that by interrupting the oxidation process and by allowing the displacement reaction to occur during an isothermal annealing in an inert atmosphere, the rate of subsequent oxidation was greatly diminished.

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Table 1: The parabolic reaction rate constant, K_p, is
shown for representative brass samples before
and after an isothermal anneal in an inert
gas. The samples were oxidized in pure oxygen
and annealed in argon at $700^{\circ}C$.

ALLOY (%Cu-%Zn)	K_p for First Oxidation Period $(gm^2/cm^4\text{-min})$	Length of Iso-thermal Anneal in Inert Gas (minutes)	K_p for Second Oxidation Period $(gm^2/cm^4\text{-min})$
70-30	9.1×10^{-10}	---	---
85-15	1.4×10^{-8} *	60	1.0×10^{-9}
85-15	1.5×10^{-8} *	120	0.5×10^{-9}
90-10	3.8×10^{-8}	120	3.2×10^{-9}
95-05	5.0×10^{-8}	---	---

* The slope at the end of the first oxidation period.

Figure 1. The percentage of copper oxide in the
oxide scale on brasses of various com-
positions oxidized in oxygen at 725°C.
Note the break in the ordinate between
30 and 70 percent.   (After Dunn)
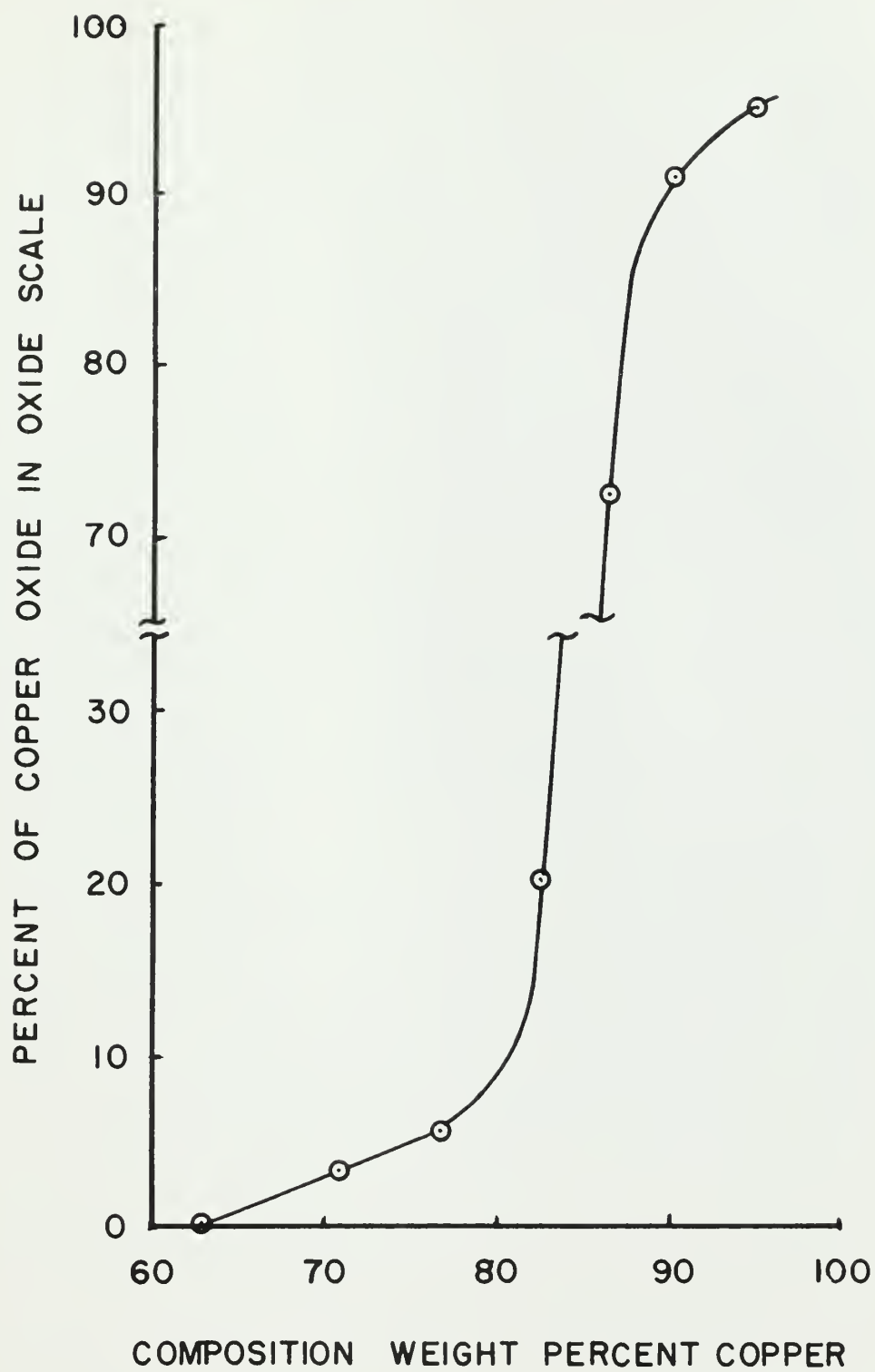
Figure 2. The influence of temperature and composition
           on the form of the oxidation rate curve.

●   Approximate conformity to the ideal oxidation law.

X   Wide departure from the ideal oxidation law.

O   Accurate conformity to the ideal oxidation law.

                                        (After Dunn)

COMPOSITION, WEIGHT PERCENT COPPER
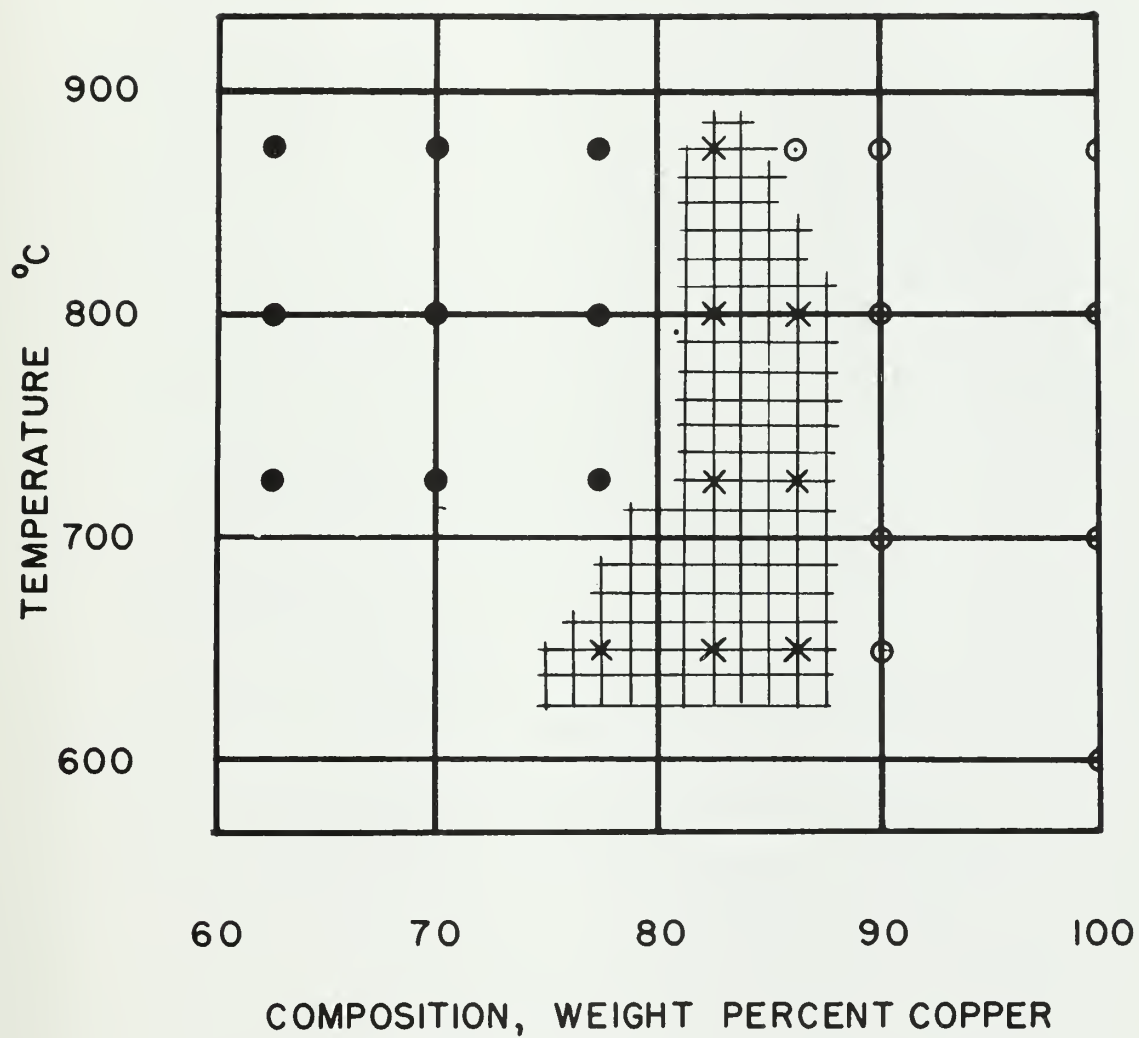
Figure 3. Schematic cross-section of the scale of an alloy

AB with an outer layer of oxide AO and an inner two-

phase layer of oxides AO and BO. At the interface

of oxides AO and BO, the displacement reaction

$$B^{+2} + 2e^- + AO = A^{+2} + 2e^- + BO$$
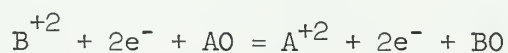
occurs so that oxide BO can grow even though it

is not in contact with the oxidizing atmosphere.

(After Wagner[4])
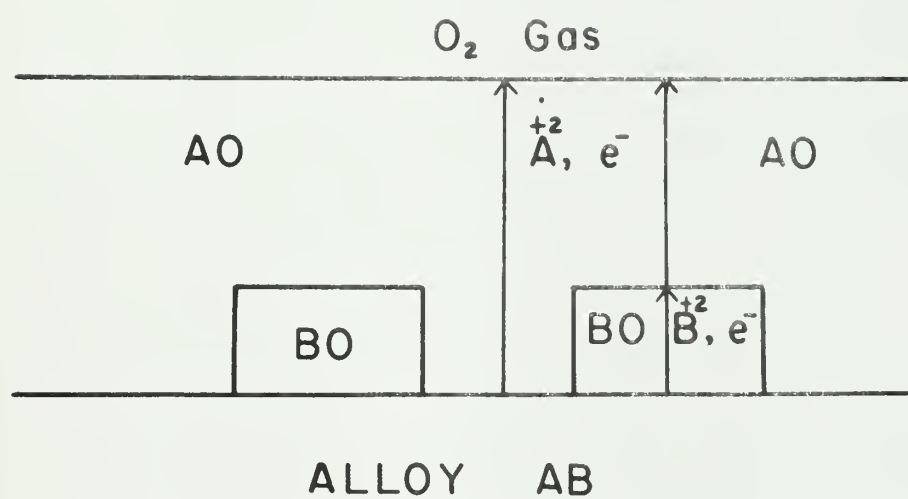
Figure 4.   Oxidation rate curve for a 70% Cu - 30% Zn alloy

oxidized in pure oxygen at 700°C.

$Kp = 9.13 \times 10^{-10}$
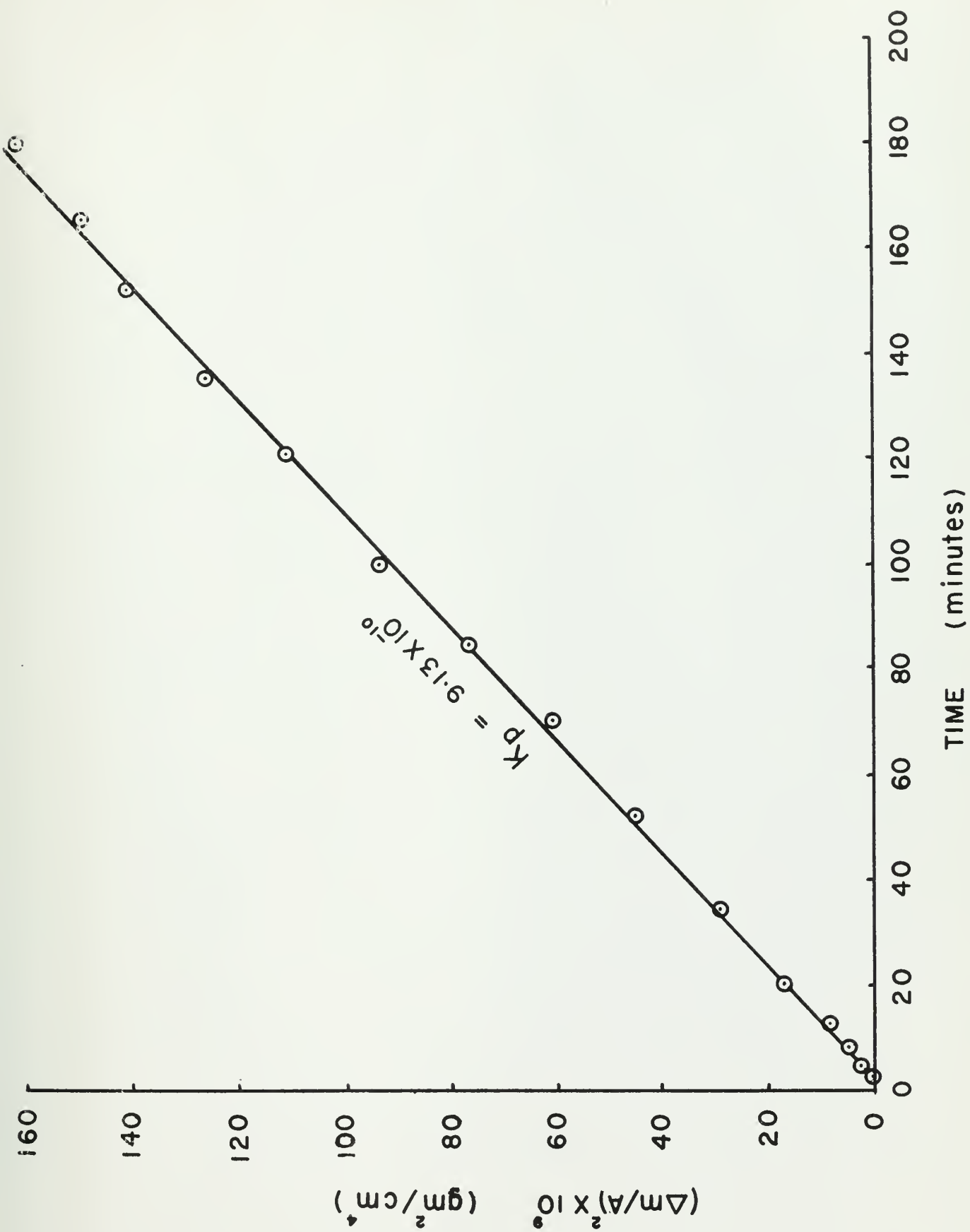
Figure 5. Oxidation rate curve for an 85% Cu - 15% Zn alloy

oxidized in pure oxygen at 700°C.
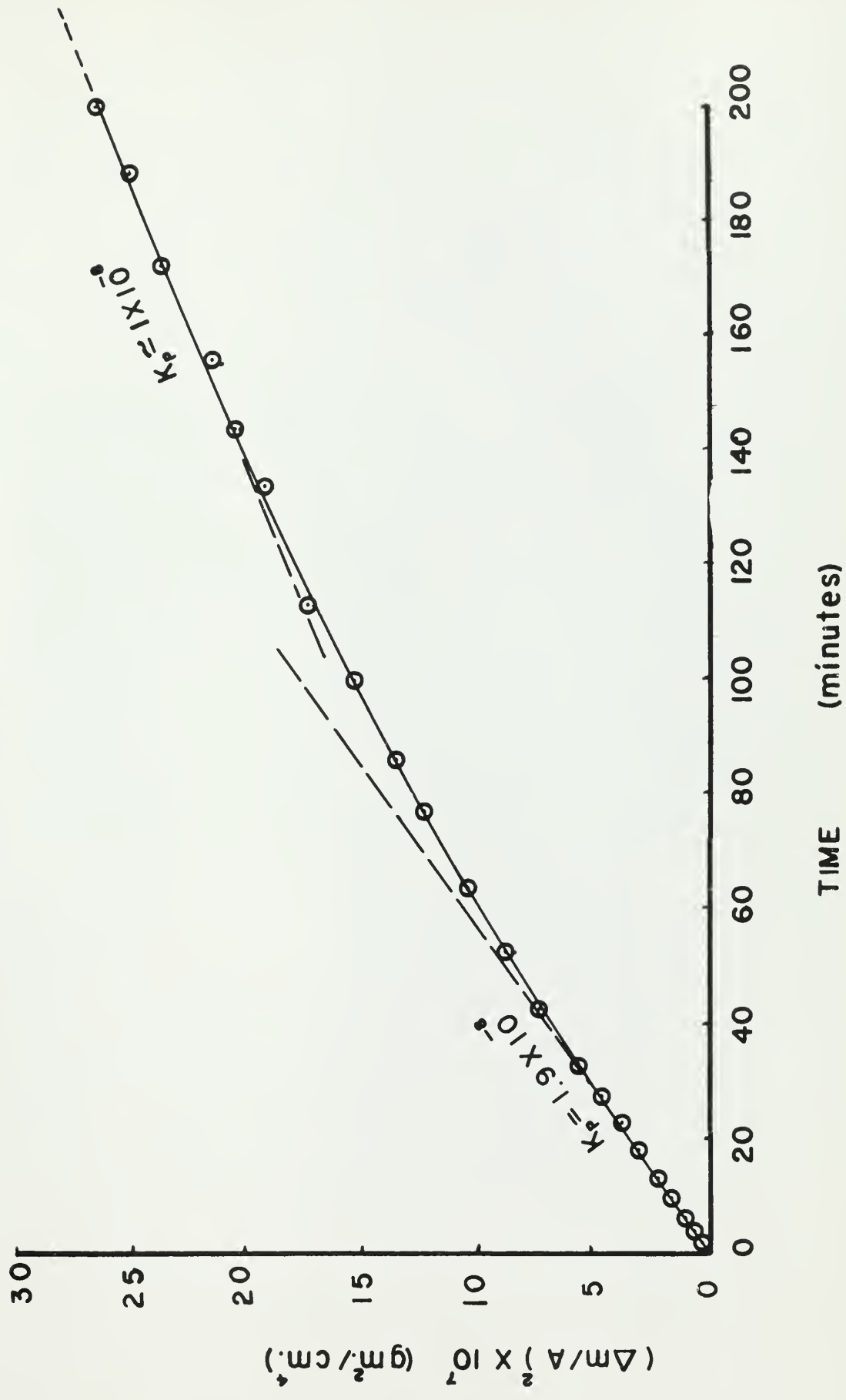
Figure 6. Cross-section of an oxide scale on an 85% Cu -
15% Zn alloy oxidized for 200 minutes in pure
oxygen at 700°C. The "pink" zinc oxide is
shown as the dark oxide layer at the metal-oxide
interface.
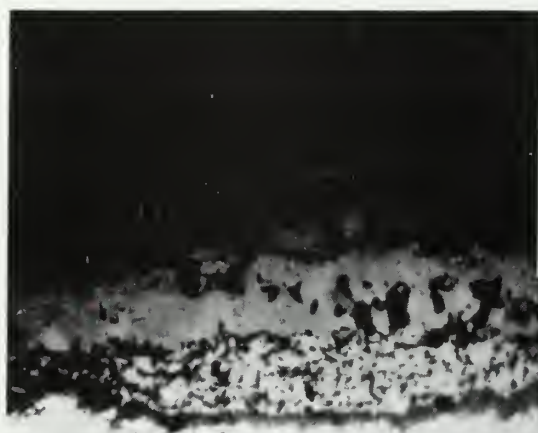
Cu$_2$O

pink ZnO

85% Cu - 15% Zn
Alloy

20μ

Figure 7.   Oxidation rate curve of an 85% Cu - 15% Zn

alloy oxidized in pure oxygen at 700°C,

interrupted by a one-hour isothermal anneal
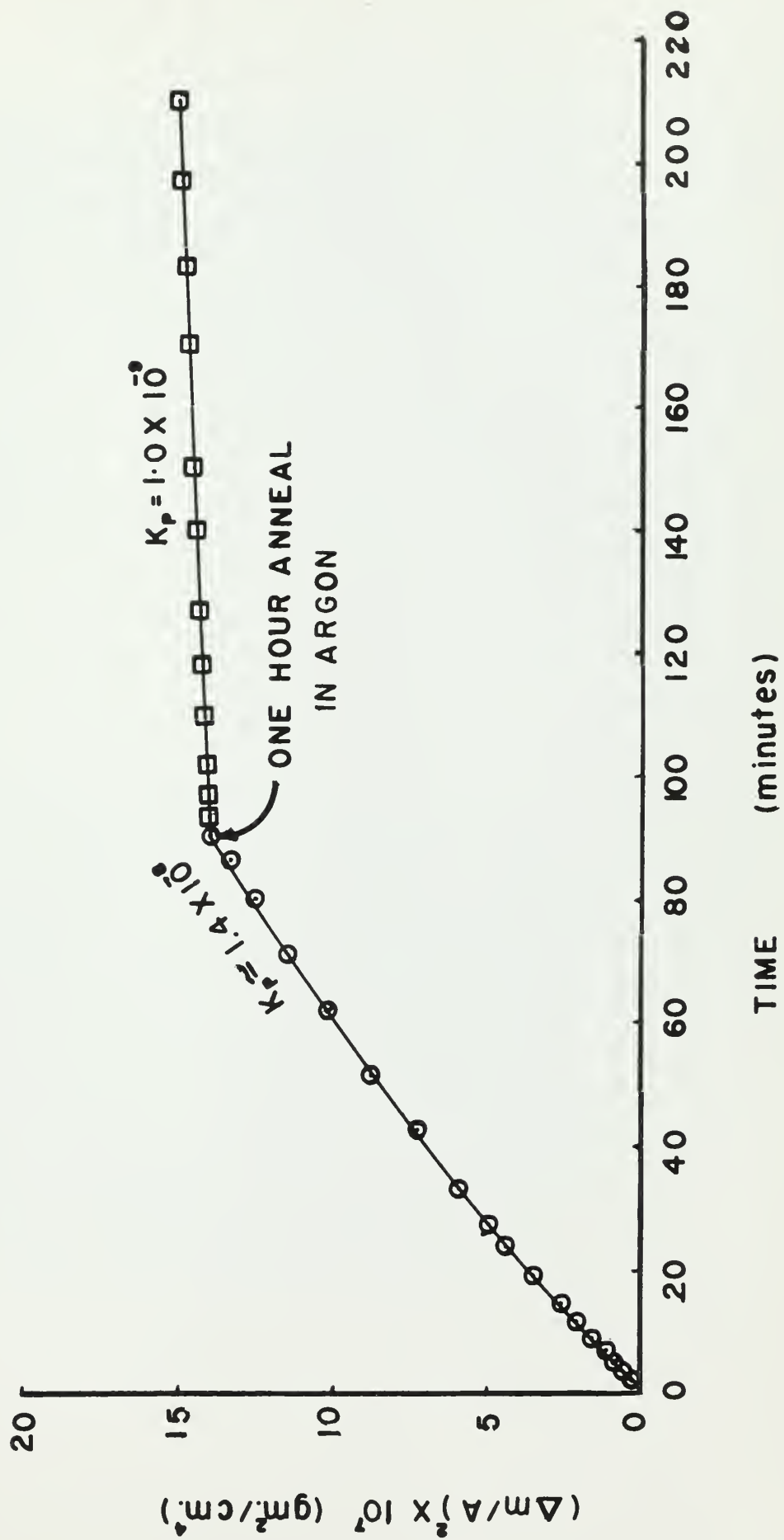
in argon.

Figure 8. Cross-sections of an oxide scale on an
85% Cu - 15% Zn alloy after a 90 minute
first oxidation period followed by a one-
hour isothermal anneal in argon followed
by a 60 minute second oxidation period.

    (a) The pink zinc oxide layer is
        thick and coherent

    (b) The pink zinc oxide structure
        remained in a dispersed state
        in a copper-red matrix.
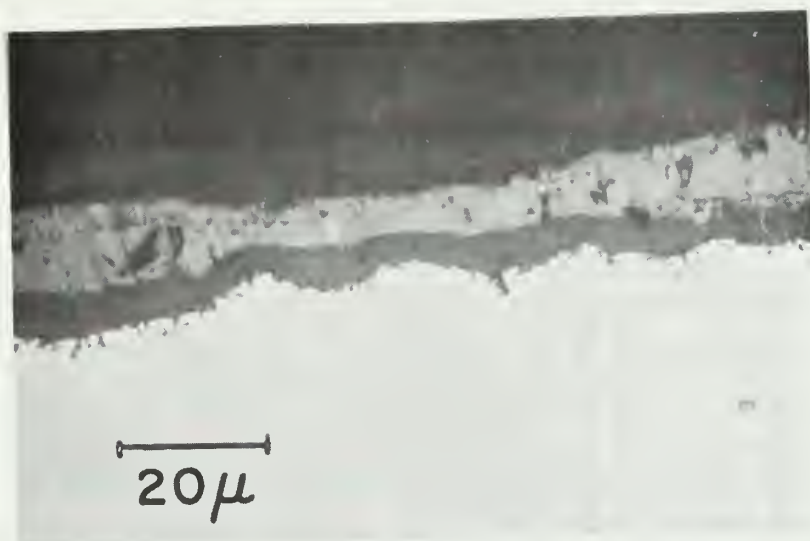
(A)

(B)

Figure 9. Oxidation rate curve for a 90% Cu - 10% Zn
            alloy oxidized in pure oxygen at 700°C,
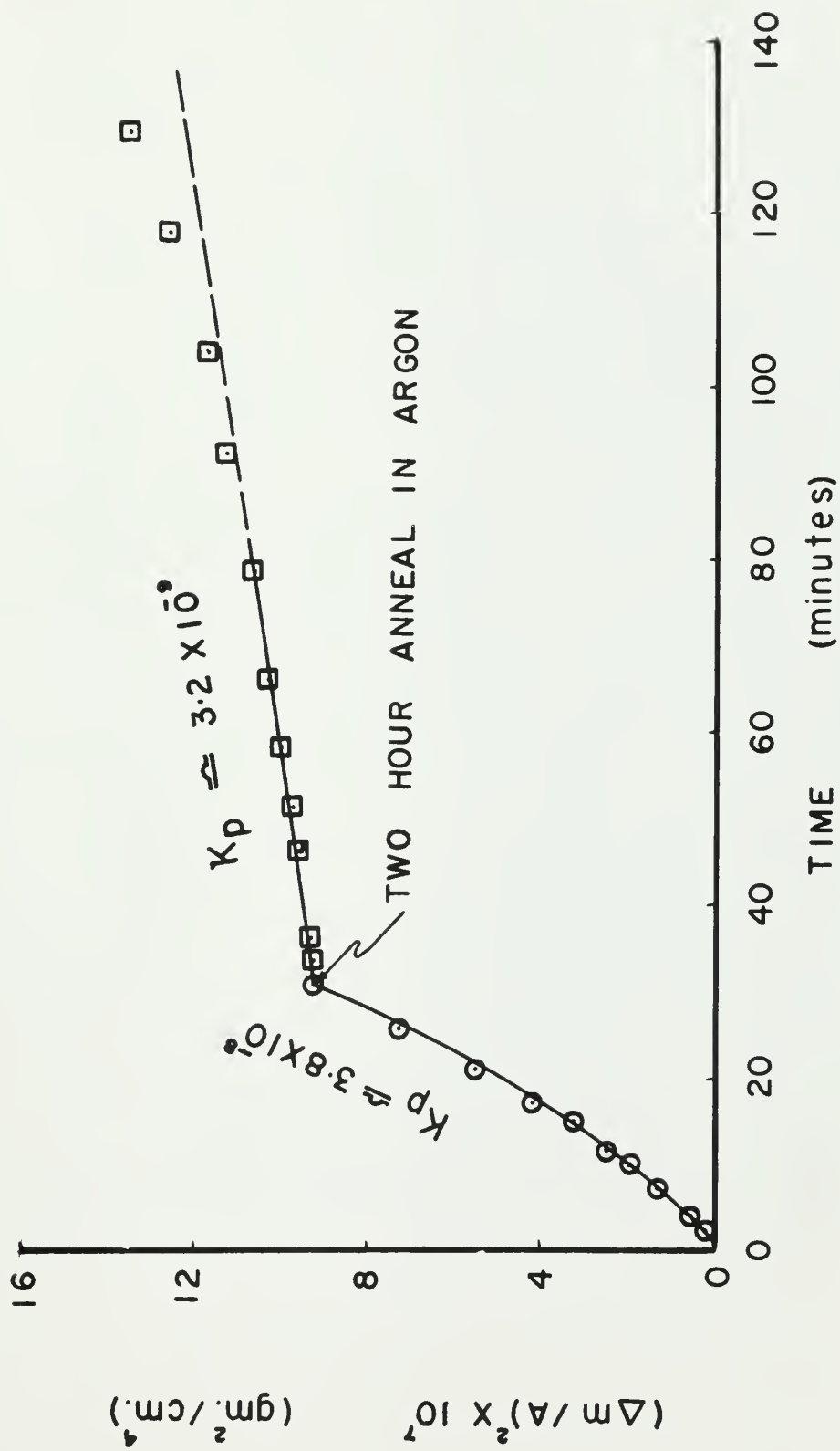   interrupted by a two-hour anneal in argon.

Figure 10. Oxidation rate curve for a 62% Cu - 38% Ni

alloy oxidized in pure oxygen at 800°C,
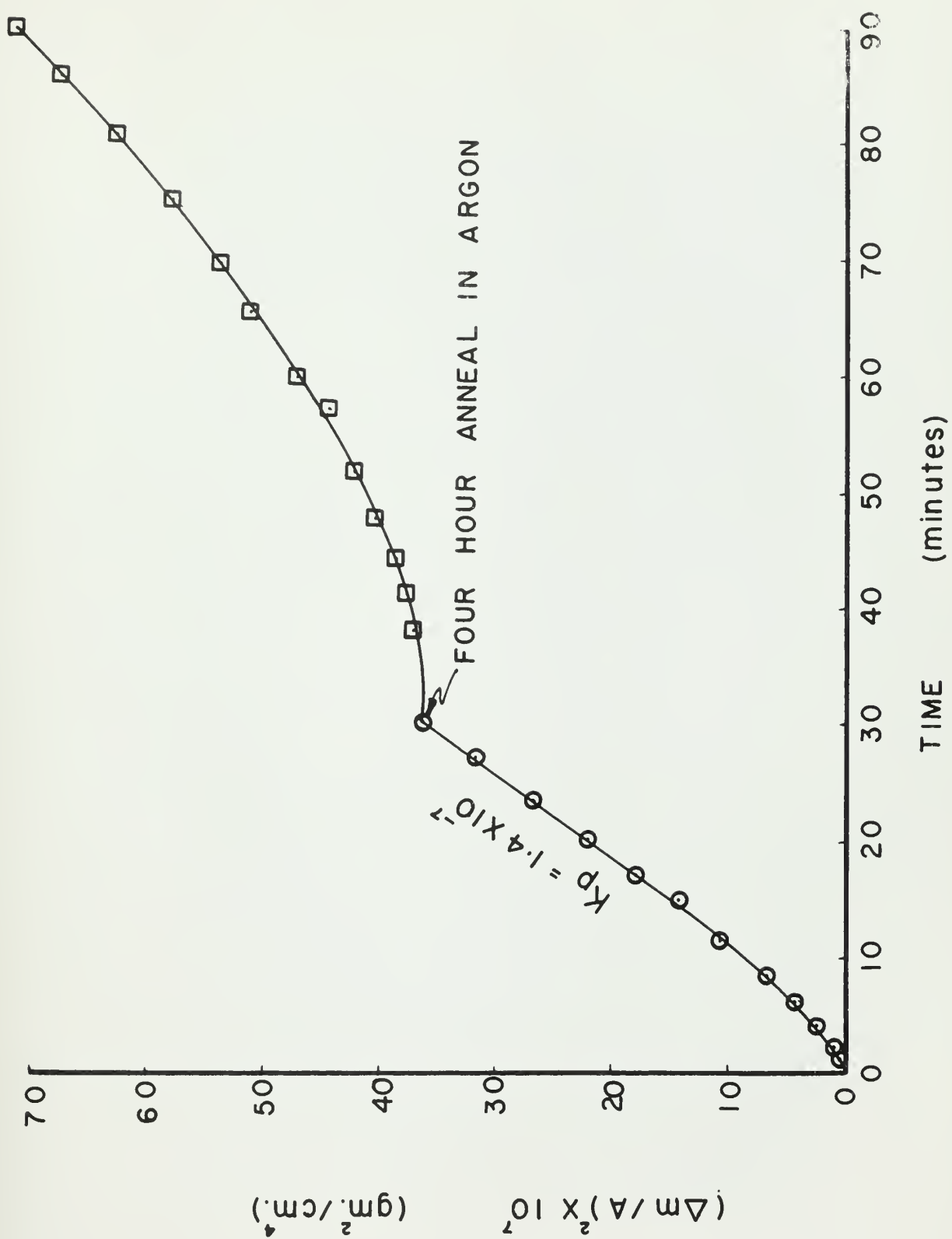
interrupted by a four-hour anneal in argon.

FOUR HOUR ANNEAL IN ARGON

$K_p = 1.4 \times 10^{-7}$

TIME (minutes)

$(\Delta m / A)^2 \times 10^7$ $(gm.^2/cm.^4)$
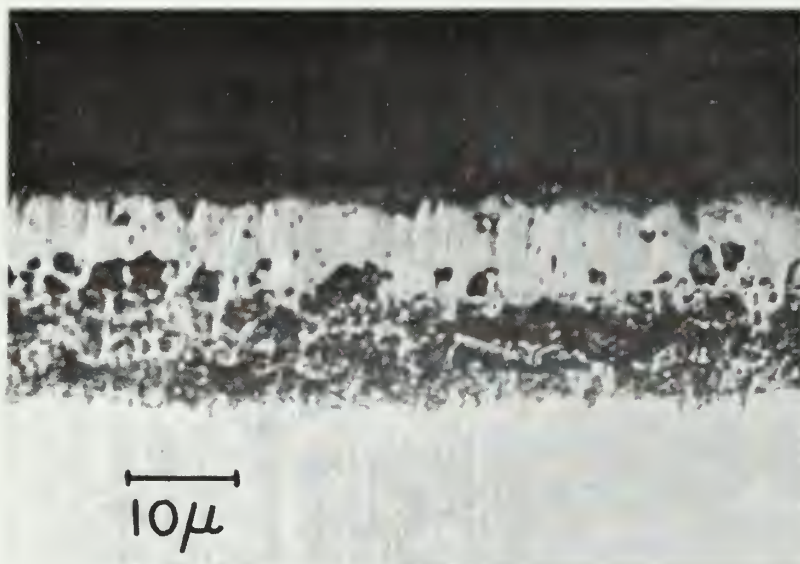
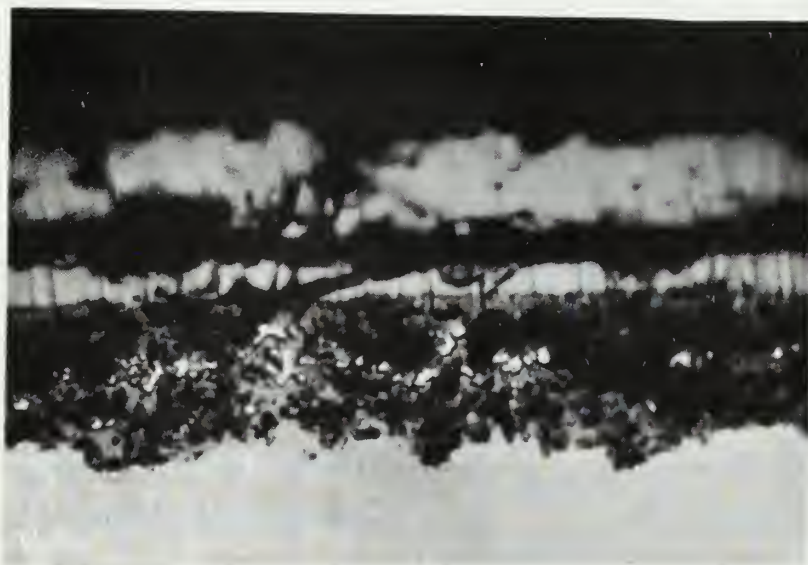Figure 11. Cross-section of an oxide scale on a 62% Cu -
            38% Ni alloy (a) after 30 minutes oxidation
            in pure oxygen at 800°C, and (b) after 30
            minutes oxidation in pure oxygen followed by
            a four-hour isothermal anneal in argon at
            800°C. Note the particles of free copper
            formed as a consequence of the displacement
            reaction.

10μ

(A)

(B)